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14. ABSTRACT Prevention or at least delay of thermal barrier coating failure is the main objective of this research, in order to increase the service lifetimes of aircraft engines. To this end, it is critical to first understand mechanisms of failure, and then use that insight to design materials countermeasures. This grant supported the following research efforts in those directions: <ul style="list-style-type: none"> <li>• Developments of a new pseudopotential theory and a solid state transition path search algorithm.</li> <li>• Applications of first principles density functional theory to: <ul style="list-style-type: none"> <li>• metal-ceramic, silicon-ceramic, and ceramic-ceramic interfaces</li> <li>• dopants placed between alumina and late transition metals, with implications for catalysis</li> <li>• fatigue in silicon and alumina</li> <li>• temperature hysteresis in the monoclinic-to-tetragonal phase transformation pathway for zirconia</li> <li>• dopants and impurities on a NiAl alloy</li> <li>• understanding the stability of early-late transition metal intermetallics</li> </ul> </li> </ul>					
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**Final Technical Report for**  
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Metal jet turbine engine components are protected by a multilayer, multi-component material known as a thermal barrier coating (TBC), comprised of a NiAl-based "bond coat" alloy onto which is deposited yttria-stabilized zirconia. A layer of alumina grows in between these two materials during zirconia deposition and grows further during engine use. If TBCs could be designed that are more robust, the engine can be run at higher temperatures, thereby achieving either increased fuel efficiency or increased thrust for the airplane. The problem with current TBCs is that after about 10,000 hrs of thermal cycling, the coatings spall and the engine must be removed from service. Preventing or at least delaying coating failure is our main objective, in order to increase the service lifetimes of aircraft engines. To this end, it is critical to first understand mechanisms of failure, and then use that insight to design materials countermeasures.

This grant supported the following research efforts in those directions:

- Developments of a new density functional theory (DFT) pseudopotential theory and a solid state transition path search algorithm.
- Applications of DFT to:
  - quantifying the interactions at and strength of metal-ceramic, silicon-ceramic, and ceramic-ceramic interfaces (in particular,  $\text{SiO}_2/\text{Ni}$ ,  $\text{ZrO}_2/\text{SiO}_2$ ,  $\text{ZrO}_2/\text{Si}$ , and  $\text{ZrSiO}_4/\text{Si}$ )
  - characterizing the role of dopants in improving adhesion between alumina and late transition metals, with implications for catalysis
  - identifying atomic level origins of fatigue in silicon and alumina

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- uncovering the origin of the temperature hysteresis in the monoclinic-to-tetragonal phase transformation pathway for zirconia
- exploring the interaction of dopants and impurities with a NiAl alloy
- understanding the stability of early-late transition metal intermetallics

We first summarize each contribution, and then present a publication list where more details of this work may be found, finally ending with a list of graduate students and postdoctorals involved in this work. The citation numbers here refer to the publication list that follows. Further details are available in earlier progress reports and in the published works cited below.

### **Advances in Condensed Matter Theory**

#### *Ultrasoft Spin-Dependent Pseudopotential Theory*

We have shown in the past that the use of spin-dependent pseudopotentials markedly enhances the transferability of the commonly used spin-neutral pseudopotential DFT method for the study of structural and magnetic properties of transition-metal-containing materials. Since the major elemental component of jet engine parts is nickel, and nickel is magnetic, accurate treatment of its magnetic behavior is essential in treating its electronic structure. Our original spin-dependent pseudopotential theory was based on the rather expensive norm-conserving pseudopotential formalism. In this latest work [7], we extended the spin-dependent pseudopotential theory for the far more computationally advantageous ultrasoft formalism and show that it is very easy to add such a feature to any pre-existing computer code. We benchmarked our new method by comparing to previously published results and then applied it to study bulk Ni, Fe, and Co, as well as a Pd atomic wire. This method will be very useful in future studies of Ni alloys, for example.

#### *Transition State Search Algorithm for Phase Transformations in Crystals*

We developed a new method to identify transition states and minimum energy paths for martensitic solid-solid phase transformations, thereby allowing the quantification of

the activation energies and identification of the atomic scale pathways of such transformations [6]. Our approach is a generalization of a previous method for identifying transition states for chemical reactions, namely the Climbing Image-Nudged Elastic Band algorithm, where we account for the global deformation of the crystalline lattice (volume and shape fluctuations) along the transition path. We also introduced an analogue to the Born-Oppenheimer approximation that allows a decoupling of nuclear motion and lattice deformation. We then applied this technique to characterize the energetics of elemental lithium phase transformations as a function of applied pressure, where we see a validation of the Born-Oppenheimer-like approximation, small energy barriers (expected for martensitic transformations), and a pronounced pressure dependence of various properties characterizing the phase transitions. This algorithm was then applied to the monoclinic-to-tetragonal phase transformation in zirconia, of significant importance to TBC failure, as described later.

### **Applications of DFT to Thermal Barrier Coating Failure**

We are interested in understanding how and why materials fail and then working to design materials where failure is delayed or inhibited completely under the desired operating conditions. To this end, we examine interfaces between ceramics and metals, in order to suggest ways to improve the stability of ceramic coatings on metals. As mentioned above, such coatings are used to protect metal components in harsh environments, including those of a jet engine. We also examine impurities and dopants that segregate at interfaces, to understand which dopants may be useful and why.

#### ***Metal-ceramic, silicon-ceramic, and ceramic-ceramic interfaces***

##### ***Silicon Dioxide as a Possible Replacement Oxide Barrier***

Our earlier work highlighted the importance of localized covalent or open-shell interactions across heterogeneous interfaces to enhance adhesion. As a result, we proposed that using a more covalent oxide in place of alumina may help adhesion of the TBC. Due to its propensity to limit bulk oxygen diffusion similar to that of alumina

(which is alumina's main purpose in the TBC), we considered silica as a possible replacement oxide [1, 2]. We find that the more covalent silica coating indeed is more strongly adhered to both interfaces that presently involve alumina. In particular, silica is predicted to bind three times more strongly to nickel than alumina does; moreover, silica does not show the dramatic falloff in adhesion with film thickness that alumina exhibits. We then examined the other interface of this proposed TBC, namely silica/zirconia, and showed that it is about twice as strongly adhered as the zirconia/alumina interface. Thus, we proposed that silica is a potential alternative oxidation barrier layer to consider as a replacement for alumina. If the zirconia layer can protect the silica from temperatures that are too high and from water, the silica should survive, and its stronger adhesion may produce a longer service lifetime of the TBC. We filed a provisional patent on this idea; a detailed search of the patent literature revealed that General Electric had already patented something similar. While we had to abandon our patent application, the GE patents lend credence to our theoretical approach to examining and designing better TBC's.

#### *Catalyst Design Based on Metal-Ceramic Interface Characterization*

Metal-oxide ceramic interfaces are not only prevalent in protective coatings such as TBC's, but are common in heterogeneous catalysis, where metal catalyst particles are bound to an oxide support. The support is typically alumina or silica, which are just the materials we have examined for TBC applications. Ni/alumina catalysts are used for all sorts of chemical processing (methanation, hydrogenation of oils for making margarine, etc.). One classic problem that catalysts have is that they often de-activate by sintering, whereby the catalyst particles aggregate together to form larger particles of low surface area. We had the idea that the sintering process might be inhibited if one could fasten more tightly the catalyst particles to the support. Hence the adhesion characterization we had done for TBC's could be applied to this completely different technology. We filed a patent on the idea that one could dope the interface between a Ni-based metal

catalyst particle and a silica or alumina support with early transition metals. The idea is that the early transition metals promote stronger oxide-metal interactions via their open shell nature, which permits donor-acceptor bonding concomitant with metal-oxo and metal-metal polar covalent bonding. We had shown this to be true for alumina/nickel interfaces and postulated it to be true for other similar interfaces in the patent application [3]. Thus the work done for the Air Force has had a spin-off to a completely different civilian technology. Engelhard Corporation, one of the major international catalyst companies, is working to test our ideas. The provisional patent application was converted into a utility patent application in June 2003 [3].

*Characterization of the Zirconia and Zirconium Silicate Interfaces with Silicon*

In the process of examining silica, zirconia, and alumina coatings on Ni and NiAl, we completed a spin-off project to characterize the electronic structure of the interfaces between  $\text{ZrO}_2$  or  $\text{ZrSiO}_4$  and Si [4]. The goal of this work was to examine whether such interfaces would be electronically suitable and stable for use in MOSFET (metal-organic-semiconductor field-effect transistor) devices. In particular, there is great interest developing alternative gate dielectrics to  $\text{SiO}_2$ , where the limit has been essentially reached in terms of minimal thickness of such layers. Go thinner, and the current in the device leaks through the insulator, shorting the device. Thus, the strategy that many are looking to exploit is to use a higher-k dielectric such that a thicker dielectric layer can be used that will have the same capacitance currently reached with silicon dioxide. Our work used DFT within the local density approximation to electron exchange and correlation, to investigate these interfaces. We considered the interface between the (001) surfaces of either tetragonal zirconia or zirconium silicate and a silicon substrate. We find that zirconia/silicon interfaces exhibit partial-filled Zr d-states, which can act as electron traps. These traps can be eliminated, e.g., by dosing the interface with hydrogen, which ties off these dangling bonds to Zr. Though the traps can be dealt with, these interfaces between zirconia and silicon exhibit asymmetric band

alignments, which is not a desirable feature in MOSFETs. By contrast,  $\text{ZrSiO}_4/\text{Si}$  interfaces exhibit no dangling bond states at the Fermi level and a much more symmetrical band alignment. These results suggest that zirconium silicate forms interfaces with  $\text{Si}(100)$  that exhibit suitable electronic properties such that  $\text{ZrSiO}_4$  may be a viable alternative gate dielectric. By contrast, our results suggest that zirconia/silicon interfaces will require further chemical treatment before they might be suitable as alternative gates in MOSFETs.

#### *Atomic Scale Fatigue in Silicon and Alumina*

In work related both to microelectronics and to TBCs, we explored the effect of cyclic tensile loading on the behavior of silicon [8] and alumina [10]. We explored the behavior of both in the threshold region of crack formation, i.e., where the crystal must choose between healing a defect through a uniform elastic strain of the material or creating two free surfaces. We find evidence for nanoscale fatigue when the silicon or alumina lattice is subjected to uniaxial tensile loading and unloading, in that defects are formed such that the crack cannot heal upon unloading. For silicon, dangling bonds are created that quickly create new Si-Si bonds to lower the surface energy, but then these new bonds are not easily broken upon unloading to form the perfect crystal again. For alumina, the atoms also rearrange significantly upon crack formation and cannot re-heal the crack perfectly, leading to a weakened crystal (i.e., fatigue). It is likely that such atomic scale fatigue impacts the durability of ceramics and semiconductors in general, since the localized bonding in both materials families requires very specific lattice structures in order to maintain cohesive strength.

#### *Monoclinic-to-tetragonal phase transformation pathway in zirconia*

It is thought that one of the modes of TBC failure could be diffusion of yttrium ions in the yttria-stabilized zirconia, leaving behind pure zirconia regions in the top coat of the TBC such that the pure zirconia may undergo phase transformations upon thermal cycling that may lead to stress buildup in the TBC (since the monoclinic phase of

zirconia is 4% larger in volume than tetragonal zirconia), eventually leading to failure. The relevant transformation takes monoclinic zirconia at ambient pressures and room temperature to tetragonal zirconia at temperatures above 1170 °C. Interestingly, t-ZrO<sub>2</sub> does not transform back to m-ZrO<sub>2</sub> at the same temperature upon cooling. It exhibits a significant hysteresis, only transforming back to monoclinic at hundreds of degrees lower temperatures. This is strongly suggestive of a kinetically or kinematically constrained and activated process. The pathway for this transformation is known to be martensitic, and therefore is a good candidate application for our new solid state transition path finder discussed above. Other than its martensite-like behavior, the atomic scale pathway that converts 7-fold coordinated Zr ions in m-ZrO<sub>2</sub> to 8-fold coordinated Zr ions in t-ZrO<sub>2</sub> is unknown. Our solid state transition state search algorithm will not only determine the activation barrier per unit cell, but will also determine the minimum energy pathway. Excitingly, the pathway we have discovered yields insights into the pronounced temperature hysteresis of the transformation [11]. First, the transformation is found to be significantly activated (6.5 meV/ZrO<sub>2</sub>) compared to activation barriers found for martensitic transformations in metals, consistent with the very high temperature required under ambient pressures for this transformation to occur. Second, we observe sudden changes in stress near the transition state with the entire transformation happening over a very small range of strain space. The temperature hysteresis may be due to the nature of transformation path, where elastic deformations of either equilibrium phase take one close to the transition state, but a stress buildup is necessary in order to overcome the barrier. This is in contrast to the situation for metals, where the stress changes are smooth and gradual. We believe the difference in behavior is due to the localized mixture of ionic and covalent bonding in zirconia, which then makes it difficult to change coordination number without this dramatic change in stress over a small strain deformation.

*Adsorption of S impurities and Hf and Pt dopants on the NiAl(110) Surface*

The key interface that appears to control spallation of TBCs is the interface between the thermally grown oxide (TGO) and the bond coat alloy. The TGO is known to be primarily alpha-alumina, which is how it is modeled in all our work. The bond coat alloy is a nonstoichiometric NiAl alloy containing either Pt in the platinum aluminide bond coats or Cr and Y in the NiCrAlY bond coat family (other elements are also added as dopants). In previous work, we modeled the bond coat alloy as pure Ni with surface dopants. We are now studying the NiAl surface, since it is thought that the surface of the bond coat alloy is enriched in Al. We study the most stable surface of NiAl, which is the most close-packed (110) surface.

The first stage of this work was to compare the structural characteristics of the clean NiAl(110) surface to experimental measurements and previous first principles theory. Here we carry out spin-polarized Kohn-Sham density functional theory, using the generalized gradient approximation (PBE-GGA) to electron exchange and correlation and the all-electron projector augmented wave (PAW) DFT method. Within this theory, static bulk structural properties (lattice parameter and bulk modulus) of NiAl are within 1% of experiment. PAW-GGA DFT also yields the experimentally determined rippling of the (110) surface, in which the Al atoms move toward vacuum while the Ni atoms move toward the bulk. These results lend confidence to the use of this method to study adsorption of relevant segregating elements on this surface.

Hf is a common dopant in the NiCrAlY bond coat alloy while Pt is a major component of the platinum aluminide bond coats (NiPtAl). S is an impurity derived from the manufacture of the Ni-base superalloy from which the aircraft jet turbine engine components are made. It is thought that S segregates to the bond coat alloy – TGO interface. Thus all three elements Hf, Pt, and S are elements of interest to characterize from the standpoint of optimizing TBCs. We have undertaken a comparison of the adsorption of these three elements on NiAl(110) [5,9]. In brief, we find that Pt and Hf prefer to bind to Ni-Ni two-fold bridge sites, consistent with STM studies by Ho and

coworkers, who have examined metal atom adsorption on NiAl(110) and found that other metal atoms (they did not examine Pt or Hf) adsorb onto the Ni-Ni bridges. By contrast, we find that S atoms are only stable in three-fold hollow sites consisting of either two Ni and one Al or two Al and one Ni. As with Hf and Pt, S shows a preference to bind to two Ni's rather than two Al's in the threefold sites.

#### *Effects of Segregating Elements on the Adhesive Strength of the TGO-Bond Coat Interface*

Now that we established the preferred adsorption sites of these elements on NiAl(110), we are characterizing the alumina/NiAl interface with and without Hf, Pt, and S present. No definitive results are available as yet. We hope these data will shed light on the role played by each of these elements in either stabilizing or destabilizing TBCs.

#### *Understanding the stability of early-late transition metal intermetallics*

Engel-Brewer intermetallics such as ZrPt<sub>3</sub> display attractive properties for advanced materials applications including high melting points, desirable mechanical properties, and oxidation resistance. The unusual stability and the preferred crystal structure of these alloys comprised of early and late transition metals were explained by Engel and Brewer through reliance on a charge transfer process by which the early transition metal actually experiences charge transfer from the late transition metal. Subsequent cluster calculations by Wang and Carter predicted the opposite trend, namely that the charge transfer was from the early to the late transition metal for these alloys. Using periodic density functional theory, we find similar results to those reported for the cluster calculations; the Pt gains electron density from Zr in the intermetallic bonding of ZrPt<sub>3</sub>. Accordingly, an understanding of the properties of these intermetallics requires significant modification to previous explanations based on the assumptions of Engel and Brewer [12].

## Summary

During the last two years, we made significant advances both in developing new methods for describing condensed matter [6, 7] and in uncovering the atomic level reasons for failure of thermal barrier coatings and of related materials [12], including fatigue [8,10] and stress buildup due to phase transformations [11] that may lead to spall. We continue to suggest how to improve them [1,2], as well thinking of spin-offs for both catalysis [3] and microelectronics [4,8]. The design principles we have proposed may help increase the stability and hence the lifetime of TBC's in the future. We continue to explore several other dopants (Hf, Pt) and impurities (S) that are known players in the evolution of TBC's during use [5,9]. Their precise roles are unclear at present; we hope to uncover the mechanisms of their actions as part of the next phase of this research.

### Publications and Patents Supported by AFOSR

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2. E. A. A. Jarvis and E. A. Carter, "Exploiting Covalency to Enhance Metal-Oxide and Oxide-Oxide Adhesion at Heterogeneous Interfaces," *J. Am. Ceram. Soc.*, **86**, 373 (2003).
3. E. A. A. Jarvis and E. A. Carter, "Catalyst Doping to Strengthen Metal-Support Interactions," foreign and U.S. utility patent conversion ongoing through UCLA.
4. R. Puthenkovilakam, E. A. Carter, and J. P. Chang, "First-principles exploration of alternative gate dielectrics: Electronic structure of  $\text{ZrO}_2/\text{Si}$  and  $\text{ZrSiO}_4/\text{Si}$  interfaces," *Phys. Rev. B*, **69**, 155329 (2004).
5. K. M. Carling and E. A. Carter, "Improving Interface Adhesion of Jet Engine Thermal Barrier Coatings," *MHPCC Application Briefs*, **14** (2004).
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8. R. L. Hayes and E.A. Carter, "Atomic Origin of Hysteresis During Cyclic Loading of Si Due to Atomic Rearrangements at the Crack Surfaces," *ChemPhysChem*, submitted (2004).
9. K. M. Carling, W. Glover, H. Gunaydin, T. Mitchell, and E. A. Carter, "Comparison of S, Pt, and Hf Adsorption on  $\text{NiAl}(110)$ ," *Surf. Sci.*, to be submitted (2005).
10. E. A. Jarvis and E. A. Carter, "Origin of Fatigue at the Atomic Scale in Alumina," *ChemPhysChem*, to be submitted (2005).

11. K. J. Caspersen and E. A. Carter, "Phase Transformation Path for Monoclinic to Tetragonal Zirconia: Origin of Temperature Hysteresis," manuscript in preparation (2005).
12. E. A. Jarvis and E. A. Carter, "First Principles Characterization of Engel-Brewer Intermetallics," manuscript in preparation (2005).

#### **Participating Graduate Students and Postdoctoral Fellows**

##### ***Graduate Students***

Emily A. Asche Jarvis, Ph.D 2002. Dissertation title: Atomic-level Culprits of Materials Failure: The Importance of Chemical Bonding at Heterogeneous Interfaces. Available from UMI Proquest Digital Dissertaions

<<http://wwwlib.umi.com/dissertations/gateway>>; all results contained in the thesis have been published in the open literature (see the list above). ACS Congressional Science Fellow 2002-03; Visiting Professor, Kenyon College, 2003-04; NRC Postdoctoral Fellow, NIST, 2005-.

Ragesh Puthenkovilakam (2003-04) - Chemical Engineering graduate student (advisor: Prof. Jane Chang).

Aaron Burns (Summer 2003); he quit graduate school in Fall 2003.

Will Glover (Spring 2004), Hakan Gunaydin (Spring-Summer 2004), and Tracy Mitchell (Summer 2004), all of whom decided to stay at UCLA when the P.I. moved to Princeton in September 2004.

##### **Postdoctoral Fellows**

Dr. Karin Carling